UCRL-94673
PREPRINT

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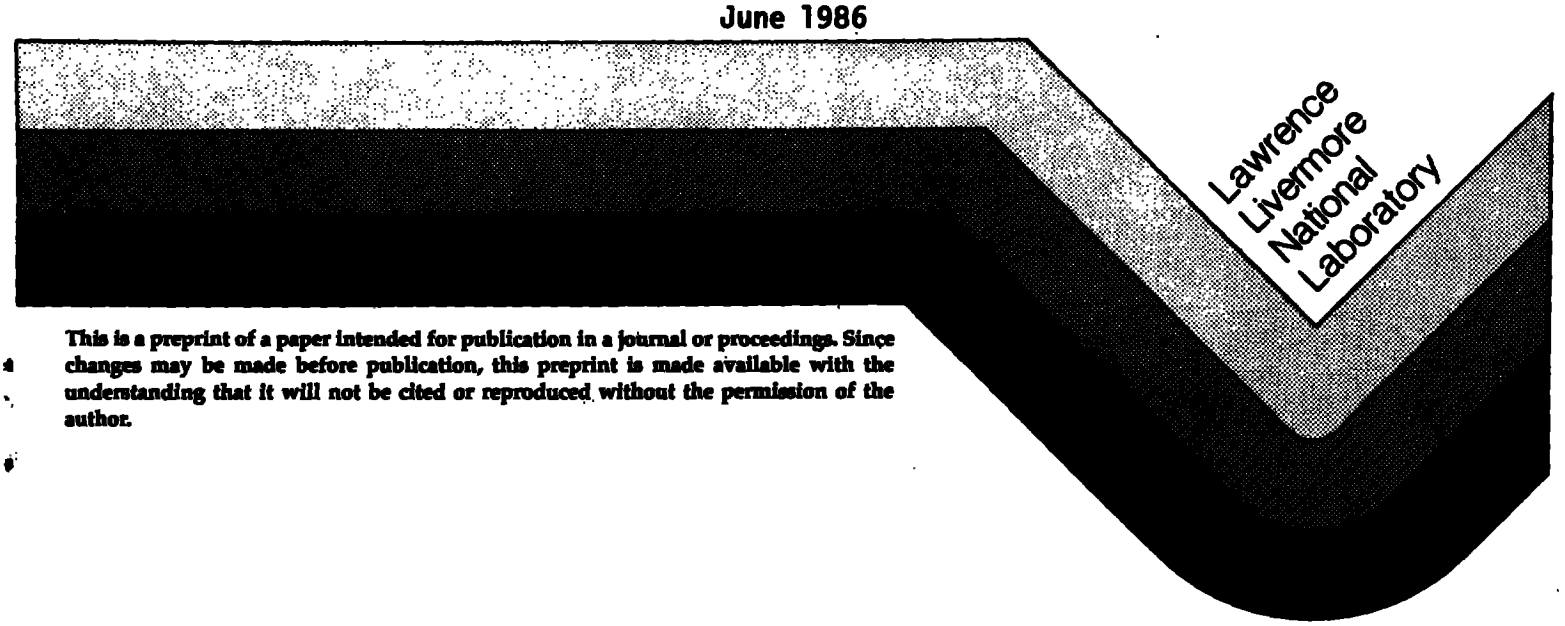
This paper was prepared for submittal to

Microchemical Journal

June 1986



Microdetermination of Organic Isocyanates and Isothiocyanates*

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The method of Vinson for the determination of organic isocyanates and isothiocyanates has been adapted to the microscale. The sample size is approximately 0.05 mequiv. This is particularly useful for high molecular-weight materials.

In the standard method for organic isocyanates and isothiocyanates, the compounds are reacted with n-butylamine in dioxane and the excess amine is then titrated with standard acid (1). This method was adapted to the microscale by Karten and Ma (2). These methods require a reaction time of about 45 min at room temperature. Vinson(3) used a dipolar aprotic solvent, N,N-dimethylformamide (DMF), and thereby shortened the reaction time to 5 min for aromatic compounds and 10 min for aliphatic compounds.

We have applied the latter method on the microscale. Using a 10-ml buret, the following parameters are suggested:

Normality of titrant: 0.01 N HCl

n-butylamine reagent: 150 mg per 100 ml of DMF

Sample size: approximately 0.05 mequiv of isocyanate (isothiocyanates)

Amount of n-butylamine reagent per sample: 5.00 ml

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*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Otherwise the procedure is the same as in the macro method (3). We favor, however, a potentiometric endpoint. It should be pointed out that the standardization of the hydrochloric acid in the original procedure is in error: The titrant should be standardized vs tris(hydroxymethyl)-aminomethane and not vs potassium acid phthalate.

Some highly fluorinated aliphatic isocyanates were not soluble in DMF. We dissolved these compounds in 1,1,2-trichloro-1,2,2-trifluorethane. The solutions were compatible with the butylamine/DMF reagent. While on addition of water 2 phases were formed, this did not interfere with the colorimetric endpoint or the electrometric endpoint when the electrodes were immersed in the aqueous phase.

Results for a proprietary fluorinated isocyanate were 4.26 ± 0.05% NCO for 4 replicates, with a standard deviation of 0.029. The corresponding isocyanate equivalent weight was 985 ± 10 for 4 replicates with a standard deviation of 4. The isocyanate equivalent weight is calculated from % NCO by (4201.7)/(% NCO).

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